The Issue of Methane Generation from In-situ Bioremediation

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Introduction

Concerns regarding methane concentrations in groundwater and air have recently been expressed to Mundell & Associates, Inc. (MUNDELL) by the Indiana Department of Environmental Management (IDEM) and the U.S. Environmental Protection Agency (U.S. EPA). MUNDELL has reviewed all available analytical data for methane generation in groundwater at the Michigan Plaza Site in Indianapolis, Indiana (the Site). Theoretical relationships between the Henry's Law Constant and equilibrium concentrations in air and water were utilized to estimate the expected methane concentrations in air as a result of the elevated methane concentrations observed in groundwater at the Site.

Estimating Air Methane Concentration from Groundwater Quality

The ratio of the aqueous-phase concentration of a chemical to its equilibrium partial pressure in the gas phase is given by the Henry's Law Constant (H):

$$H = \frac{C_{air}}{C_{water}}$$

The dimensionless Henry's Law Constant for Methane is 30 (Hartman, 1998). The highest methane concentration observed in groundwater at the Michigan Plaza Site is ***25,000 ug/L***. This concentration was observed at MMW-P-03D during the February 4, 2010, quarterly groundwater sampling event.

Using the above relationship and assuming:

$$H = 30$$

$$C_{water} = 25{,}000 \frac{ug}{L}$$

$$C_{water} * H = C_{air}$$

$$C_{air} = 30 * 25{,}000 \frac{ug}{L}$$

The theoretical concentration of methane in air due to the concentration observed in groundwater is:

$$C_{air} = 750{,}000 \frac{ug}{L} \; or \; 0.750 \frac{g}{L}$$

The lowest explosive limit (LEL) is defined as the gas or vapor in air capable of producing a flash of fire in presence of an ignition source. At a concentration in air below the LEL there is not enough fuel to continue and explosion. At *25 ^{o}C*, the LEL for Methane is *5.1%* by volume (*51,000 ppmV*). To compare

our calculated methane concentration in air with the LEL, we must convert from *0.750 g/L* to parts per million by volume. The conversion is as follows:

$$ppmV = C * \frac{1}{Molecular\ Weight} * 8.3144\ \frac{L\ kPa}{mol\ {}^{o}K} * T * \frac{1}{P}$$

Where:

$C = 0.750 \frac{g}{L}$

$Molecular\ Weight\ (CH_4) = 0.016048 \frac{g}{mol}$

$T = 298.15\ {}^{o}K$

$P = 101.325\ kPa$

$$ppmV = 0.750 \frac{g}{L} * \frac{1}{0.016042 \frac{g}{mol}} * 8.3144\ \frac{L\ kPa}{mol\ {}^{o}K} * 298.15\ {}^{o}K * \frac{1}{101.325\ kPa}$$

$$ppmV = 0.750 \frac{g}{L} * \frac{1}{0.016042 g} * 8.3144\ L * 298.15 * \frac{1}{101.325}$$

$$\boldsymbol{ppmV = 1,143.8}$$

Comparing the theoretical concentration of methane in air (*1,143.8 ppmV*) and the LEL for methane at *25^{o}C* (*51,000 ppmV*) indicates that air concentrations at the Site relative to the maximum observed methane concentration in groundwater are approximately **2% of the accepted LEL**. In addition, no significant observations of airborne methane have been noted at the Site during previous groundwater sampling events.

Published literature related to the generation and degradation of cis-1,2-dichloroethylene in groundwater and methanogenesis during bioremediation (Kean et al., 2003) has indicated methane concentrations as high as 125,000 ug/L in groundwater can occur from maximum cis-1,2-DCE accumulation prior to further breakdown to vinyl chloride. Based on this level, maximum methane concentrations in air immediately above the groundwater are not expected to exceed 10 % of the accepted LEL for methane. Based on the relationship between cis-1,2-DCE accumulation and methane generation, MUNDELL expects to observe elevated levels of dissolved methane only as long as the cis-1,2-DCE continues to be generated. As cis-1,2-DCE concentrations decline as vinyl chloride is generated, dissolved methane concentrations will also decline.

Dangerous levels of methane in air generated by in-situ reductive dechlorination processes have not been documented in any literature sources reviewed by MUNDELL. Theoretical calculations based on Henry's Law indicate methane concentrations in air due to the dissolved methane in groundwater at the Site will be approximately 2% of the published LEL. Based on the above, MUNDELL does not see a need to proceed with methane air screening at the monitoring wells and structures at the Site unless otherwise directed.

REFERENCES

Hartman, B., 1998, “Oh Henry! (a constant),” LUSTLine Bulletin 29, pp. 17-18.

Kean, J. A., Graves, D., and Lodato, M., 200X, “Enhanced Reductive Dechlorination and the Relationship between Cis-1,2-DCE Accumulation and Methanogensis,” State Coalition for Remediation of Drycleaners, Regenesis, San Clemente, CA.